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Laser Action from 2,6,8-Trisubstituted-1,3,5,7-Tetramethyl-pyrromethene-BF_2 Complex: Part 1

by

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Laser action from 2,6,8-position trisubstituted 1,3,5,7-tetramethylpyrromethene-BF_2 complexes: part 1

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Of the four new pyrromethene derivatives studied, 1,3,5,7,8-pentamethyl-2,6-diethylpyrromethene-BF_2 complex lased ~3 times more efficiently than rhodamine 560 under flashlamp excitation.

For obtaining efficient laser action under flashlamp excitation, the coumarin (blue to yellow/green) and xanthene (yellow to red spectral region) laser dyes are presently the most widely used. Among the xanthene laser dyes, the benchmark of laser dyes in efficiently and photostability is rhodamine 6G. This dye has been known since 1967[1] and was found by trial and error.

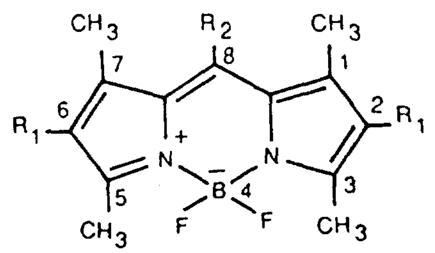
Recently, laser action under flashlamp excitation was reported from 1,3,5,7-tetramethylpyrromethene-BF_2 complex 1 (TMP-BF_2) and 1,3,5,7,8-pentamethylpyrromethene-BF_2 complex 2 (PMP-BF_2). TMP-BF_2 lased broadband (BB) somewhat more efficiently than coumarin 545A at 533 nm,[2] and PMP-BF_2 lased BB ~3 times more efficiently than coumarin 545 at 546 nm.[3] To change the spectral and, therefore, the laser action properties of a pyrromethene-BF_2 complex (4,4-difluoro-4-bora-3*a*,4*a*-diaza-*s*-indacene), we performed substitutions in the 2-, 6-, and 8-positions of the pyrromethene-BF_2 molecule while maintaining the four methyl groups in the 1-, 3-, 5-, and 7-positions.

For testing, the same small dye laser was used as in Ref. 4. Its highest input energy was 10 J from an EG&G FX139C-2 flashlamp, producing a pulse ~600 ns long at the halfwidth and having an ~200-ns rise time. The laser output energy was measured with a Scientech model 365 power/energy meter. The spectroscopic equipment used to measure the triplet extinction coefficients ϵ_T of the new laser dyes was the same as in Ref. 5. McClure's method was used.[6] The fluorescence spectra and quantum fluorescence yields Q_F were measured with a Perkin-Elmer Corp. LS-5B luminescence spectrometer. The visible/UV absorption spectra of the dyes were recorded with a Cary 17 spectrophotometer.

The synthesis of the four substituted pyrromethene-BF_2 complexes 3–6 will be reported elsewhere. Rhodamine 575 was purchased from Exciton and rhodamine 110 (rhodamine 560) from Eastman Kodak Co. Methanol (99.9% spectroscopic grade) was obtained from Aldrich Chemical Co., ethyl alcohol (190 proof punctilious) from Quantum Chemical Corp., USI Division, and 2-methyltetrahydrofuran from Lancaster Synthesis, Ltd.

Table I. Quantum Fluorescence Yield Q_F, Fluorescence Intensity Maximum λ_F, Absorption (S–S) Intensity Maximum λ_S, (S–S) Absorption (Extinction) Coefficient ϵ_S, and Laser Action Wavelength λ_{las} of the Pyrromethene Complexes 3–6

Complex	Q_F	λ_F(nm)	λ_S(nm)	log ϵ_S	λ_{las}(nm)
3	0.70	544	518	4.83	566
4	0.83	547	518	4.86	567
5	0.35	530	493	5.00	556
6	0.31	533	494	4.62	559



(1) $R_1 = R_2 = H$ (TMP-BF_2); (2) $R_1 = H, R_2 = CH_3$ (PMP-BF_2); (3) $R_1 = R_2 = CH_3$ (HMP-BF_2); (4) $R_1 = C_2H_5, R_2 = CH_3$; (5) $R_1 = CO_2C_2H_5, R_2 = C_2H_5$; (6) $R_1 = NO_2, R_2 = CH_3$.

1,2,3,5,6,7,8-heptamethylpyrromethene-BF_2 complex 3 (HMP-BF_2) showed laser action BB at ~566 nm when dissolved in a 2×10^{-4}-M solution of ethyl alcohol. Laser action wavelength (BB) and other spectroscopic data are collected in Table I; 2×10^{-4} M was about the upper limit of solubility in methyl or ethyl alcohol of the new laser dyes we studied. When methyl alcohol was used as a solvent, HMP-BF_2 lased only 2/3 as efficiently as in ethyl alcohol.

Because rhodamine 560 exhibits laser action BB at ~570 nm (in a 2×10^{-4}-M solution in ethyl alcohol), it was used for comparison. Note, however, that rhodamine 560 cannot be labeled as an efficient or very stable xanthene laser dye. We, therefore, also used rhodamine 575 (in a 2×10^{-4}-M solution in ethyl alcohol) as a standard. It showed laser action BB at 579 nm. This dye can be grouped among the better xanthene laser dyes in efficiency and photostability.

As is apparent from Fig. 1, HMP-BF_2 lases about twice as efficiently as rhodamine 560 and ~10% more efficiently than

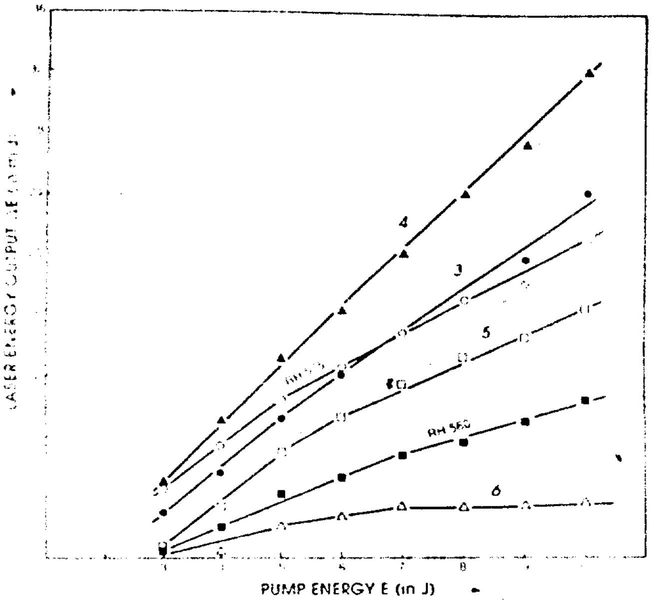


Fig. 1. Laser energy output ΔE (mjoules) as a function of flashlamp pump energy E (joules) of 2×10^{-4} M solutions of rhodamine 560 (RH 560), rhodamine 575 (RH 575), and the complexes 3 and 4 dissolved in ethyl and 5 and 6 in methyl alcohol.

rhodamine 575. HMP-BF_2 and rhodamine 575 showed comparable photostability.

1,3,5,7,8-pentamethyl-2,6-diethylpyrromethene-BF_2 complex 4 exhibited efficient laser action in a 2×10^{-4}-M solution in ethyl alcohol. In methyl alcohol, it lased with about 2/3 the effifiency shown in the ethyl alcohol solution. From the experimental results shown in Fig. 1, complex 4 lased ~3 times more efficiently than rhodamine 560 and ~50% more efficiently than rhodamine 575. Compared with rhodamine 6G,[3] it lases ~10% more efficiently.[3] Complex 4 and rhodamine 575 showed about the same photostability.

To obtain the ϵ_T values, we used the 514.5-nm line from an ion-argon cw laser for excitation. Noteworthy is the exceptionally low ϵ_T value of complex 4 over the fluorescence (laser action) spectral region. This $\epsilon_T(567) = 1.5 \times 10^3$-liter/mole cm value was similar to that obtained for PMP-BF_2 (reported in Ref. 3) and appears to be the key factor in the remarkable laser action properties of the pyrromethene-BF_2 laser dyes. We have $\epsilon_T(570) = 7.9 \times 10^3$ liter/mole cm for rhodamine 560 (Ref. 7) and $\epsilon_T(580) = 6.6 \times 10^3$ liter/mole cm for rhodamine 575.[8] It is probable that complex 4 lases with a higher efficiency than HMP-BF_2 because of its higher Q_F value.

1,3,5,7-tetramethyl-8-ethyl-2,6-dicarbethoxypyrromethene-BF_2 complex 5. This dye lased with considerably less efficiency than dyes 3 and 4, which is not surprising considering its low Q_F value. Nevertheless, this new dye lases with higher efficiency than rhodamine 560 (Fig. 1). The data in this figure were obtained from a 2×10^{-4}-M solution in methyl alcohol, where the dye lased ~10% more efficiently than observed from a solution in ethyl alcohol.

1,3,5,7,8-pentamethyl-2,6-dinitropyrromethene-BF_2 complex 6. This compound is an oddity among laser dyes, because it exhibits laser action under flashlamp excitation—although not very efficiently. It is well known that aromatic nitrocompounds rarely show fluorescence; however, in a few cases weak fluorescence has been noted. Heretofore, nitrocompounds were not known to show laser action under flashlamp excitation. Complex 6 was routinely prepared in investigating P-BF_2 chemistry. Because it showed some fluorescence ($Q_F = 0.31$), we tested its ability to lase. Photochemically, the compound was unstable. Therefore, the values for Q_F and λ_{las} shown in Table I are not too accurate.

In summary, of the four new dyes we tested, complex 4 easily surpassed rhodamine 560 in efficiency and rivals rhodamine 6G as one of the most efficient of the laser dyes. Other 2,6,8-position trisubstituted pyrromethene-BF_2 complexes should either lase in different spectral regions or possess different laser/physical properties, e.g., efficiency, solubility (water), and photostability. Employing these new laser dyes should result in improved performance (increased average power output) in dye lasers.

Over the last few years, it has been stated that dye lasers do not have much of a future compared with the exceptional performance of the newly developed solid state devices like Ti:sapphire and diode lasers. This may be the case for small dye lasers. However, when tunability, high average power operation, and visible laser light output at low cost are required, a large flashlamp pumped dye laser operating with improved laser dyes should be difficult to beat.

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